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**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of: DAVID CHARLES ADAMS, ET AL. : Docket: ADN2653P1US  
Serial No.: 09/778,192 : Examiner:  
Filing Date: February 7, 2001 : Group Art Unit: 1744  
For: Closed Loop Continuous Polymerisation :  
Reactor and Polymerisation Process :

Assistant Commissioner for Patents  
Washington, D.C. 20231

**SUBMISSION OF CERTIFIED PRIORITY DOCUMENT**

Sir:

Enclosed herewith is a certified copy European Patent Application No.; 98202666.8, to support the claim of foreign priority benefits under 35 U.S.C. §119 in connection with the above-identified application.

Respectfully submitted,



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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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**Blatt 2 der Bescheinigung  
Sheet 2 of the certificate  
Page 2 de l'attestation**

Anmeldung Nr.: 98202666.8  
Application no.: 98202666.8  
Demande n°:

Anmeldetag:  
Date of filing: 07/08/98  
Date de dépôt:

Anmelder:  
Applicant(s):  
Demandeur(s):  
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Bezeichnung der Erfindung:  
Title of the invention:  
Titre de l'invention:  
Closed loop continuous polymerisation reactor and polymerisation process

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:	Tag:	Akkordzeichen:
State:	Date:	File no.
Pays:	Date:	Numéro de dépôt:

Internationale Patentklassifikation:  
International Patent classification:  
Classification internationale des brevets:  
B01J19/18, B01J19/24, C08F2/00

Am Anmeldetag benannte Vertragstaaten:  
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/

Etats contractants désignés lors du dépôt:

Bemerkungen:  
Remarks:  
Remarques:

Closed loop continuous polymerisation reactor and polymerisation process.

The invention pertains to a closed loop continuous emulsion polymerisation reactor at least comprising a circulation pump, a reactor tube which

5 connects the outlet of the circulation pump to its inlet, at least one feed for supplying raw materials, an outlet, and preferably means for cooling or heating the tube.

Such a process is known from, int. al., M. Wilkinson and K. Geddes, "An

10 award winning process," Chemistry in Britain, pp. 1050-1053, December 1993. This publication describes that emulsion polymers are manufactured by addition polymerisation of low molecular weight unsaturated monomers, in the presence of water and stabilisers. In the past, the polymerisation was carried out as a batch process or a delayed addition batch process, but in

15 15 the late sixties the closed loop continuous reactor was first developed.

A problem encountered in polymerisation processes employing a tubular reactor is the formation of deposits from the reaction products on the internal wall of the reactor. These deposits lead to a need for an increased

20 delivery pressure from the circulation pump and impair heat transfer from the reaction medium to, e.g., a coolant in a jacket surrounding the reactor tube, thus leading to higher (and often deleterious) reactor temperatures or necessitating either an increased coolant circulation rate, a lower coolant temperature, or a reduced rate of production (so as to match the heat

25 removal).

A further general disadvantage of a fouled reactor is the reduction of volume, increasing both the recycle rate and the shear on the emulsion. This shifts the process conditions which may have been optimised on a

30 clean reactor. In any case product properties will drift, nullifying the advantages of consistency of production expected from continuous reactors.

One way of cleaning the inside of tubes or pipework is the use of a cleaning member or pig which is forced through the tube. German patent application 32 33 557, for instance, describes various ways of using a pig for cleaning

- 5 the internal wall of a tubular reactor. In one embodiment (illustrated in Fig. 1 of the said application), two ball valves are provided in the reactor tube for receiving and launching one or more pigs. The reaction product is used to drive the pig and leaves the reactor after the pig has passed the outlet. Thus, the reaction product is not and cannot be recirculated, rendering this
- 10 configuration unsuitable for continuous polymerisation. In a further embodiment (fig. 3), spherical-shaped scraper pigs are passed through the pump. This method imposes severe limitations on the shape of the pig and the type of pump used. For instance, the use of a positive displacement type pump to give the low shears desirable for emulsion polymer production
- 15 is not possible.

The invention has for an object to realise a continuous polymerisation reactor employing a pig, which allows simple removal of the pig from the reactor without the necessity of shutting down the polymerisation process,

- 20 which affords great freedom in selecting the type of circulation pump and material and shape of the pig, and which enables total control over the launching of the pig substantially independent of the reaction medium flow. This is achieved by use of a reactor of the type described in the opening paragraph, which further comprises an additional tube for by-passing a pig
- 25 around the circulation pump, a pig receiving station which is in parallel connection with the circulation pump or the reactor tube, and optionally means for directing the pig into the pig receiving station.

- 30 By the present idea, pigging can be fully automated and the pig can be replaced either during operation, simply by opening up of the pig receiving station without the flow of the reaction medium being disturbed, or during normal (weekly) maintenance, whichever is considered desirable. More

importantly, however, the presence of a pig does no longer limit the range of suitable circulation pumps, allowing the use of, e.g., pumps which impose low shear on the reaction medium. Also, the shape and material of the pig can be fully optimised for the reactor tube employed and the nature of the 5 deposits.

The fact that the pig receiving station is not part of the main reactor tube and that the pig is actually removed from the reactor medium flow (as opposed to, e.g., remaining between two ball valves in the main flow) 10 enables the operator of the reactor according to the present invention to launch the pig as and when he sees fit.

For completeness' sake, it is noted that US 3,425,083 discloses an endless pipe which has a bent form allowing a cleaning member to circulate 15 constantly through the pipe and past its inlet and outlet for a liquid medium. The outlet has a smaller capacity than the inlet, so that part of the liquid medium is returned from the outlet through a return portion of the pipe to and past the inlet for recycling. No means are provided for removing the cleaning member or for interrupting its circulation. Further, the said pipe is 20 intended for heating liquids like milk and not for cooling reacting emulsions. In fact, reactors are not mentioned at all.

US 3,682,186 discloses an apparatus for by-passing scrapers or product displacers around a pipeline booster or compression station. The main line 25 is provided with two check valves for receiving and launching the pig. Loop reactors are not mentioned.

Although the station may take the form of a side track somewhere in the loop reactor, it is preferred that the pig receiving station is integrated into 30 the additional tube for by-passing a pig around the circulation pump. This can be achieved (comparatively) easily if the reactor tube is in fluid communication with the suction side of the circulation pump through an

aperture in its wall and continues on to the delivery side of the circulation pump, the part of the tube between the said suction and delivery sides of the circulation pump serving as a pig receiving station.

- 5 Once the pig approaches the suction side of the pump, it is led into the pig receiving station, allowing the emulsion to pass behind it into the circulation pump. The pig is then halted in the receiving station, where it remains until it is launched for the next cleaning cycle.
- 10 A significant advantage of this embodiment resides in the launch opening of the pig receiving station being positioned very close to the delivery side of the circulation pump, thus providing maximum thrust during the launching of the pig and improving the reliability of the launching system.
- 15 The pig can be launched using, e.g. in the case of polymerisation of vinyl monomers in aqueous suspension, either the emulsion in the reactor or the water phase feed. Instead of a diversion of the water phase to launch the pig, a controlled "shot" of water or some other compatible fluid could be used to launch the pig.
- 20 In the reactor according to the present invention it is preferred that the said aperture through which the reactor tube is in fluid communication with the suction side of the circulation pump is a slot extending substantially in the longitudinal direction of the tube. When the pig passes this slot, the force
- 25 driving it is automatically lifted. It is further preferred that the width of the slot is smaller than the width of the pig, because, in that case, no additional means like a mesh or bars are required for directing the pig into the pig receiving station and to prevent the pig from leaving the tube.
- 30 It was found that by using a tapering slot of which the width increases downstream, the danger of fouling near the slot is reduced and the pressure in front of the pig can be kept to a minimum while at the same

time sustaining ample pressure behind the pig to drive it into the pig receiving station.

The closed loop reactor according to the present invention preferably

- 5 comprises a reactor tube of which at least a substantial part forms a helical coil. In comparison to the common trombone arrangement of the continuous tube (as disclosed in, e.g., M. Wilkinson and K. Geddes, "An award winning process," Chemistry in Britain, pp. 1050-1053, December 1993) the shape is more appropriate for pigging in that the pig is not forced
- 10 to make sharp turns, thus reducing the wear of the pig and allowing the use of longer pigs. Furthermore, uncooled joints, which are one of the origins of wall fouling, can be avoided by using a helically coiled continuous tube.

The invention further pertains to a process for preparing (emulsion) polymers by means of the closed loop reactor described above. It is preferred that a pig is launched at intervals ranging from approximately 1 to approximately 60 minutes, preferably from approximately 10 to 20 minutes. Apart from more effective cleaning of the tube walls, regular disturbance of slow moving or static layers of emulsion polymer close to the tube walls will

- 15 prevent or at least delay the onset of a poorly heat conducting stationary outer layer of polymer.
- 20

Some typical commercial monomers suitable for use in the present polymerisation process include, e.g., butyl acrylate, methyl methacrylate, styrene, vinyl acetate, Veova 9, Veova 10, Veova 11 (all three ex Shell), ethyl acrylate, 2-ethyl hexyl acrylate, ethylene, and vinyl chloride. The addition reaction is initiated by radicals to give a dispersion of high molecular weight polymer particles usually of 50 to 3000 nm diameter suspended in a medium in which the polymer is insoluble, usually water.

- 25
- 30 Common free radical generators include the sodium, potassium, and ammonium salts of peroxodisulphuric acid, e.g. ammonium peroxodisulphate. Alternatively, redox couples can be used. These consist

of an oxidising agent and a reducing agent. Commonly used oxidisers are the salts of peroxodisulphuric acid and t-butyl hydroperoxide and hydrogen peroxide itself. Reducers are sodium sulphite, sodium metabisulphite, sodium formaldehyde sulphonylate, and sodium dithionite.

5

Polymerisation of monomers in aqueous suspension is preferred and, in that case, raw materials are preferably provided by separate feed streams. These streams introduce fresh monomer and an aqueous solution of stabilisers known as the water phase or, e.g., a pre-emulsion of monomer 10 and water and an aqueous solution in a separate small stream. The reactor is filled at the start of the reaction with water phase made up in a solution tank. Other fillings are possible, particularly with finished emulsion polymer (of the same or different composition) from a previous run, "as is" or diluted to any concentration; water; or an alternative special water phase used for 15 the filling and possibly for the early stage of the run.

Agitation in the reactor is provided by the in-line circulation pump. Shortly after the feed streams start to flow, the monomers begin to react and heat is liberated. The temperature is stabilised by cooling means, usually by 20 controlled circulation of a cooling fluid (e.g. water) through a cooling jacket. The product flows to the cooling tank where residual monomer converts to polymer. After cooling, the emulsion polymer is filtered to remove any oversize particles or gritty material in the strainer and transferred to the product storage tank.

25

Within the framework of the present invention, the term "pig" comprises any element suitable for removing deposits and the like from the inner wall of tubular reactors and being carried through the reactor with the fluid stream. Other common terms for such an element are, e.g., "scraper" and "cleaning 30 member". Pigs usually consist of soft or semi-hard natural or synthetic material, e.g. rubber or polyurethane. Also, pigs or scrapers with (flexible) metal parts or metal brushes as well as combinations of metal and a soft or

semi-hard natural or synthetic material can be used. Of the numerous possible shapes, cylinders, cylinders with round edges as well as cylindrical bodies with thick lips and/or thick strips on the outer circumference are preferred. Dumb-bell shaped cylindrical pigs have two scraping surfaces, as

5 opposed to spherical surfaces which have only one. Also, the front scraping surface is (or can be) a leading edge scraper. A spherical pig has only one trailing edge.

The design of the pig and the materials used depend, among other things,

10 on the type of deposit and the tolerances and radii of the reactor tube. Incidentally, it is noted that the amount of wear of the pig can be determined from the time needed for one cleaning cycle (a worn pig will require more time to complete a cycle). Preferred circulation pumps are, int. al., positive displacement pumps.

15 The invention will now be illustrated by means of two unlimitative examples.

Figure 1 shows schematically a closed loop reactor in accordance with the invention. Prior to pigging, the reaction mixture flow is around the reactor

20 tube 16. Water phase flows to the reactor 16 via valve 12, with valve 15 closed. Product overflows through the cooling tank line from the reactor via three-way valve 13 with valve 14 closed. The procedure to launch and receive the pig is as follows: 1) Check by means of the pig detector that the

25 pig is correctly located in the pig station; 2) open valves 11 and 15, close valve 12; 3) after 15 seconds, open valve 12 and close valves 15 and 11; 4) open valve 14; 5) change valve 13 so that the flow of product is via valves 14 and 13; 6) observe arrival of the pig into the pig station by means of the pig detector, and 7) switch valve 13 so that the flow of product is direct and close valve 14.

30 Pig removal is carried out as follows: 1) close valves 11, 14, and 15; 2) split "quick release" couplings A and B; 3) remove the section of the pipework

(i.e., the pig station); 4) remove the pig for inspection and replace if necessary, and 5) reassemble couplings A and B.

Figure 2 shows schematically a further embodiment in accordance with the present invention. Again, prior to pigging, the reaction mixture flow is around the reactor tube 27. Product flows to the cooling tanks through none of the valves shown. Water phase enters the circulation pump below valve 25 and is not shown in this figure. Valves 21, 22, 23, and 24 are closed and valve 25 is open when no pigging procedure is being carried out. The procedure to launch and receive the pig is as follows: 1) Check by means of the pig detector that the pig is correctly located in the pig station; 2) open valve 21; 3) open valve 22, if pressure is insufficient to launch the pig, partially close valve 26 until the pig launches successfully; 4) after pig launching, open valve 26 fully and close valves 21 and 22; 5) after 15 seconds, open valves 24 and 23; 6) check that the pig has returned to the pig station after, e.g., 1 minute, if the pig has not been detected within the desired time, partially close valve 25 until a signal on the pig detector is registered, and 7) open valve 25 fully and close valves 23 and 24.

## Claims

1. A closed loop continuous emulsion polymerisation apparatus at least comprising a circulation pump, a reactor tube which connects the outlet of the circulation pump to its inlet, at least one feed for supplying raw materials, and an outlet, characterised in that the reactor further comprises an additional tube for by-passing a pig around the circulation pump and a pig receiving station which is in parallel connection with the circulation pump or the reactor tube.
- 10 2. The polymerisation apparatus according to claim 1, wherein the pig receiving station is integrated into the additional tube for by-passing a pig around the circulation pump.
- 15 3. The polymerisation apparatus according to claim 2, wherein the reactor tube is in fluid communication with the suction side of the circulation pump through an aperture in its wall and continues on to the delivery side of the circulation pump, the part of the tube between the said suction and delivery sides of the circulation pump serving as a pig receiving station.
- 20 4. The polymerisation apparatus according to claim 3, wherein the aperture is a slot extending substantially in the longitudinal direction of the tube.
- 25 5. The polymerisation apparatus according to claim 4, wherein the width of the slot is smaller than the width of the pig.
- 30 6. The polymerisation apparatus according to claim 5, wherein the width of the slot increases downstream.

7. The polymerisation apparatus according to any one of claims 1 to 4, wherein the reactor comprises means for directing a pig into the pig receiving station.
- 5 8. The polymerisation apparatus according to any one of the preceding claims, wherein at least a substantial part of the reactor tube forms at least one helical coil.
9. A process for preparing emulsion polymer by means of the polymerisation apparatus according to any one of the preceding claims.
10. The process according to claim 9, wherein a pig is launched at intervals ranging from 1 to 60 minutes, preferably from 10 to 20 minutes.

**Abstract**

The invention pertains to a closed loop continuous emulsion polymerisation apparatus at least comprising a circulation pump, a reactor tube which 5 connects the outlet of the circulation pump to its inlet, at least one feed for supplying raw materials, an outlet, and means for cooling the tube, characterised in that the reactor further comprises an additional tube for bypassing a pig around the circulation pump, a pig receiving station which is in parallel connection with the circulation pump or the reactor tube, and 10 optionally means for directing a pig into the pig receiving station. The invention allows simple removal of the pig from the reactor, afforts great freedom in selecting the type of circulation pump and material and shape of the pig, and enables total control over the launching of the pig substantially independent of the reaction medium flow.

15

TO COOLING TANKS

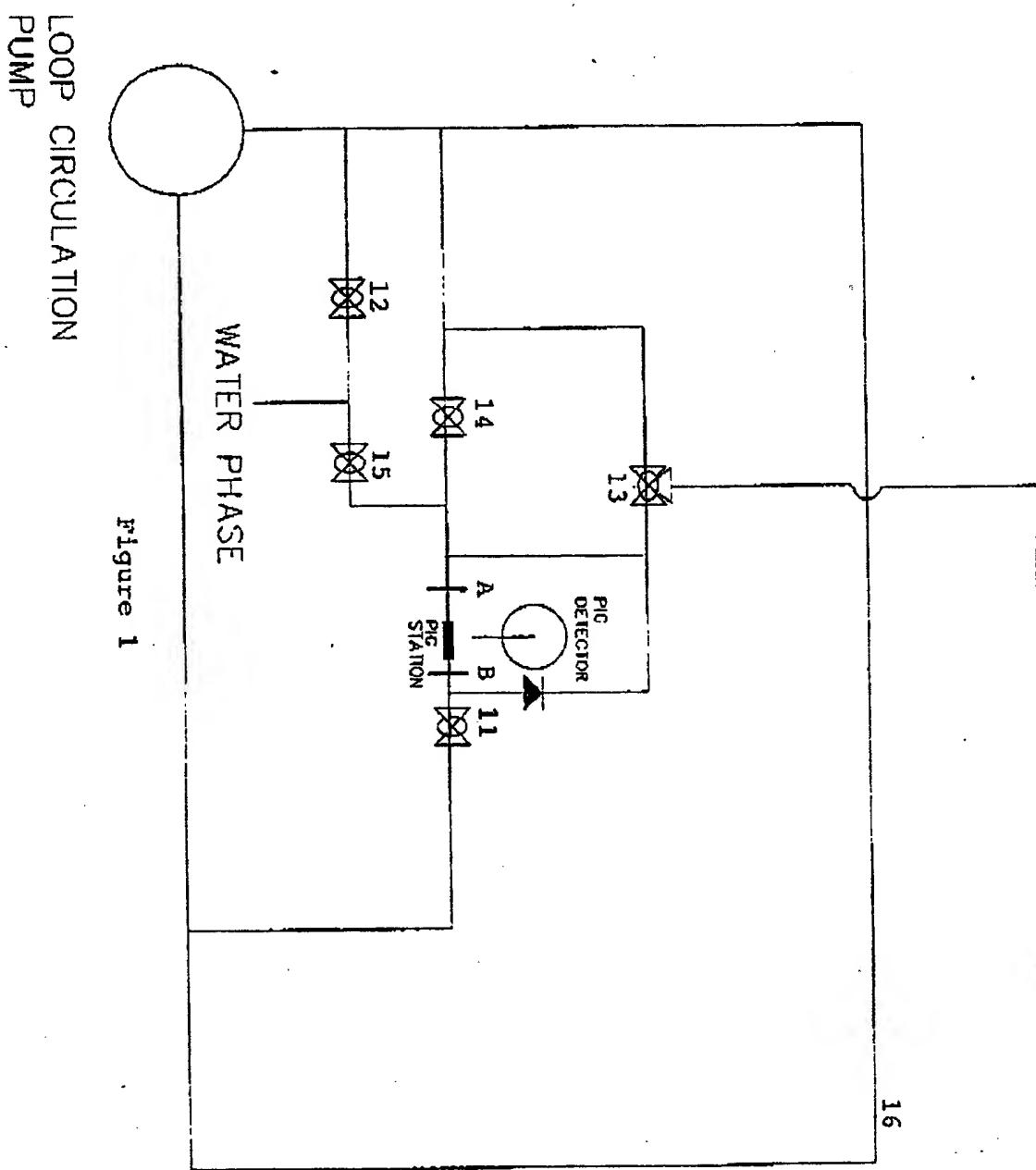


Figure 1

TO COOLING TANKS

27

PIG  
DETECTOR

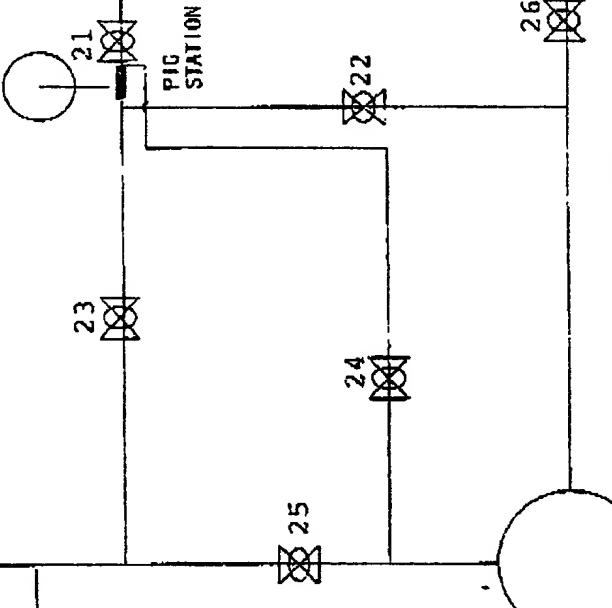


Figure 2

LOOP CIRCULATION  
PUMP